Allyl Butyl Ethers[1]

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It has been suggested that in our work on allyl starch,[2] one of the butyl alcohols might serve as a reaction solvent. The obvious objection to the use of alcohols in this reaction is the formation of ethers at the expense of allyl halide used for the main reaction. When an attempt was made to separate the allyl butyl ethers by fractionation of the organic layer of the reaction, azeotropes of the ether and alcohol were obtained.[3] Since attempts to separate the two by extracting the butyl alcohols with water were unsuccessful, at least in the case of normal and isobutyl alcohols, it was deemed advisable to learn more about the properties of pure allyl butyl ethers. In the literature, only the allyl isobutyl ether has been reported.[4] It was prepared by catalytic dehydration of a mixture of the two corresponding alcohols. The boiling point (108–110°) was the only property given. We have, therefore, prepared the four allyl butyl ethers and determined some of their properties.

(1) Contribution from one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) P. L. Nichols, Jr., R. M. Hamilton, Lee T. Smith and E. Yanovsky, *Ind. Eng. Chem.*, **37**, 201 (1945); E. A. Talley, R. M. Hamilton, J. H. Schwartz, C. A. Brown and E. Yanovsky, U. S. Dept. Agr., Bur. Agr. and Ind. Chem., AIC-140, (Eastern Regional Research Laboratory) Feb. 1947 (Processed).

(3) *Cf.* D. N. Kursanov and O. M. Shemyakina, *Doklady Akad. Nauk S. S. S. R.*, **62**, 341–343 (1948); *C. A.*, **43**, 2159*b* (1949).

(4) A. Mailhe and F. de Godon, *Bull. soc. chim.*, [4] **27**, 328 (1920).

Experimental

Preparation and Properties of Allyl Butyl Ethers.—All ethers were prepared in the same manner. One to one and a half moles of butyl alcohol in 200 to 300 cc. of xylene was placed in a 1-liter three-necked flask furnished with a condenser, a stirrer and a separatory funnel. An equimolar quantity of sodium was gradually added to the solution. After the entire amount of sodium had been added, the reaction slowed down somewhat owing to coating of alkoxide on the metal. At this point, the bath temperature was raised to about 115° and the stirrer was started. The sodium melted, and the reaction proceeded. After all the sodium had disappeared, the flask was cooled to room temperature, and an equimolar amount of allyl bromide was gradually added through the separatory funnel. When the entire amount of allyl bromide had been added, the bath temperature was raised to 110–115° and kept at this temperature for about five hours. If any blue color remained at this time, methanol was added until the blue color disappeared. The mixture was then washed with water, dried and distilled. The theoretical amounts of allyl bromide were used for convenience of procedure at the expense of better yields. Under the conditions of the experiments, the yields were about 25% for the allyl *t*-butyl ether, 40% for the ether of isobutyl alcohol and 60% for the ethers of normal and secondary butyl alcohols.

Table I gives the properties of the four ethers.

Table I

Properties of Allyl Butyl Ethers

Butyl group	Allyl (by Wijs), % (theory, 36.0%)	B.p., °C.	Mm.	d^{20}_4	$n^{20}D$	Mole refraction Calcd.[a]	Found
Normal	36.0	117.8–118.0	763	0.7829	1.4057	35.87	35.80
Secondary	36.0	107.1–107.4	762	.7792	1.4023	35.70	35.70
Iso	36.0	106.6–107.0	749	.7735	1.4008	35.90	35.85
Tertiary	36.1	99.2–100.0	760	.7770	1.4011	35.83	35.71

[a] A. I. Vogel, *J. Chem. Soc.*, 1842 (1948).